

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 March 2004 (25.03.2004)

PCT

(10) International Publication Number
WO 2004/024684 A2

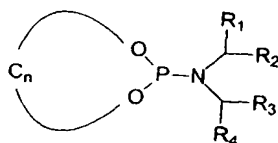
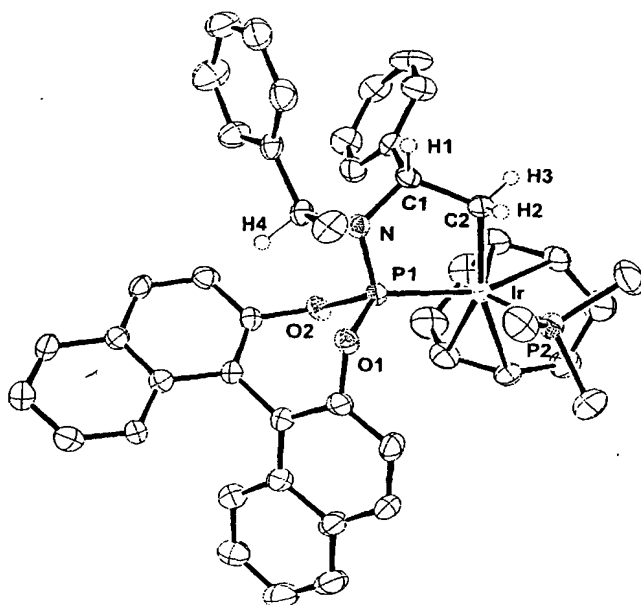
- (51) International Patent Classification⁷: **C07D**
- (21) International Application Number:
PCT/US2003/028718
- (22) International Filing Date:
12 September 2003 (12.09.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/410,407 13 September 2002 (13.09.2002) US
60/445,154 5 February 2003 (05.02.2003) US
- (71) Applicant (for all designated States except US): **YALE UNIVERSITY** [US/US]; Two Whitney Avenue, New Haven, CT 06511 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **HARTWIG, John, F.** [US/US]; 46R Stephens Wood Lane, Durham, CT 06422 (US). **SHU, Chutian** [US/US]; 100 Deepwood

Drive, Hamden, CT 06517 (US). **OHMURA, Toshimichi** [JP/JP]; Kitakasuga-cho 235-1, Apt. 105, Ooharano, Nishikyo-ku, Kyoto 610-1152 (JP). **KIENER, Christoph** [DE/DE]; Kalmitstrasse 20, 67256 Weisenheim am Sand (DE). **LOPEZ, Fernando, Garcia** [ES/ES]; San Pelayo 38-40, A Estrada Pontevedra, e-36680 (ES).

- (74) Agent: **GARABEDIAN, Todd, E.**; Wiggin & Dana LLP, One Century Tower, P.O. Box 1832, New Haven, CT 06508-1832 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),

[Continued on next page]

(54) Title: ENANTIOSELECTIVE AMINATION AND ETHERIFICATION



(57) Abstract: The present invention is directed to a catalyst composition, comprising: (1) a catalyst precursor having the general structure MSX_n wherein M is a transition metal selected from the group consisting of iridium, molybdenum, and tungsten; S is a coordinating ligand; X is a counterion; and n is an integer from 0 to 5; and (2) a phosphoramidite ligand having the structure wherein O-C_n-O is an aliphatic or aromatic diolate and wherein R₁, R₂, R₃ and R₄ are selected from the group consisting of substituted or unsubstituted aryl groups, substituted or unsubstituted heteroaryl groups, substituted or unsubstituted aliphatic groups, and combinations thereof, with the proviso that at least one of R₁, R₂, R₃, or R₄ must be a substituted or unsubstituted aryl or heteroaryl group. The present invention is also directed to activated catalysts made from the above catalyst composition, as well as methods of allylic amination and etherification using the above catalysts.